FINAL REPORT

METHODOLOGY FOR MEASUREMENT OF HEAT OF HYDRATION OF NON-FERROUS SLAG BINDERS

by

E.E. Berry

Work on this project was conducted under the auspices of the Canada Centre for Mineral and Energy Technology, Energy, Mines and Resources, Canada.

DSS FILE NUMBER: 27SQ.23440-3-9095
DSS CONTRACT SERIAL NUMBER: OSQ83-00092
CANMET SCIENTIFIC AUTHORITY: Dr. E. Douglas.

Date November 20th, 1983.

MICROMEDIA

13 pp

E. E. BERRY
& Associates

SUITE 350
130 SLATER ST.
OTTAWA, ONTARIO

1. Introduction.

Sources of non-ferrous slags in Canada that are produced in significant quantities are the copper, nickel and lead producing industries [1]. Quenched slags from these industries have been examined as low-grade supplementary cementing materials for such applications as mine backfill and waste stabilization.

It is of interest in determining the manner in which such slags contribute to the cementitious activity of hydraulic systems to examine the course of their hydration as it occurs. One tool for such investigation is the conduction calorimeter. Its use is becoming increasingly common in the study of the mechanism and kinetics of cementing processes.

This report is concerned with the practical application of conduction calorimetry to the determination of heats of hydration of blended cements and supplementary cementing materials based on non-ferrous slags. In addition some consideration is given to the research applications of conduction calorimetry in as much as they are extensions of the methodology employed to determine simple heats of hydration.

The report takes the form of a bibliographic review of some major published sources. The first section comprises a short introduction to the theoretical basis for the application of calorimetry to the study of cement hydration followed by consideration of some of the types of conduction calorimeter available to the cement chemist. The final section presents a detailed consideration of the Wexham Instruments conduction calorimeter which offers a particularly suitable means to obtain integrated heats of hydration without the complications introduced by the use of more precise and sensitive instruments.

2. Cement Hydration and Calorimetry.

The hydration reactions that are responsible for the development of cementitious activity in hydraulic binders are exothermic. Because the reactions are heterogeneous; subject to retardation and acceleration by the action of products and co-reactants; and present distinctly different kinetic characteristics, it is possible to study the dynamics of cement hydration in real-time through examination of the rate at which the evolution of heat proceeds.

Skalny and co-workers [2,3] have discussed in detail the hydration processes relevant to the hardening of portland and other cements, including a complete discussion of the relationships between heat evolution and the chemical processes of hydration.

Figure 1 shows in schematic form the relationship between rate of heat evolution and time for the progress of cement hydration. The main features of such rate of heat evolution curves are the relative magnitudes and the position on the time axis of each of three rate peaks (A,B and C in Figure 1) the origins of which have been discussed by a number of authors [2,3,4,5,6,7]. Peak A is not usually resolved in experiments with the more simple forms of conduction calorimeter. It results from the heat evolution occuring on mixing cement and water, which is consequent upon a complex combination of events including solution of alkalies and gypsum, the heat of wetting of the solid phases, hydration of free lime and the formation of ettringite. The measurement of these processes is also overshadowed by the thermal changes occuring due to the establishment of temperature equality between the sample and the calorimeter (this is probably the dominant process and has been addressed, largely unsuccessfully, by a number of researchers).

The second and major peak, B, occurs with portland cements after 6 to 12 hours of hydration. It is ascribed to the continued formation of ettringite and, mainly to the early stages of hydration of C_3S. Cements with elevated levels of C_3A may exhibit a third peak, C, ascribed to the conversion of ettringite to mono-sulphoaluminate. After the appearance of this final peak, the rate of heat evolution declines reaching a small and decreasing value thereafter. The area under the curve is a measure of the total heat of hydration of the complex system and in practice may be determined by integration of the curve.

The thermal effects measured by calorimetry are of practical as well as theoretical interest in that the construction of large mass concrete structures requires that the heat generated be dissipated rather than permitted to raise the temperature of the hydrating mass which may cause cracking of the structure. It is normal practice to control this thermal process by selection of a cement said to exhibit a low heat of hydration. Although this is a practical solution, and cements showing low heat of hydration properties as determined by adaptations of the Hess method[8] are available, in fact what is required is not only a low total heat of hydration, but also a slow rate of release of that heat, ie. a slow rate of hydration. This is the case because the setting of concrete is rarely an isothermal process and it is the rate of temperature rise that is of concern, not the total heat liberated.

One means of controlling the rate of temperature rise is to include supplementary cementing materials in the cement being used. Figure 2 shows the way in which the addition of a supplementary cementing material can influence the rate of heat evolution as revealed by conduction calorimetry. It is clear

that although the total heat of reaction may be unaffected by the addition of the supplementary cementing material the net rate of heat evolution at the time when portland cement is reacting most rapidly is reduced and in favorable circumstances it may be assumed that the gross temperature increase would also be reduced. For the purposes of evaluating the practical application of cements, this characteristic of the calorimetric curve is probably its most valuable feature.

The calorimeter has one further application in cement studies, as a tool to estimate the energies of activation, E_a of the hydration reactions, and hence in principle to measure the relative reactivity of cement components. As an instrument to estimate E_a the conduction calorimeter can be applied if a number of rather extended assumptions are made as follows.

If it is assumed that the instantaneous rate of heat evolution is proportional to the rate of a particular reaction then measurement of the maximum rate of heat evolution for that reaction (ie. the height of an assigned peak) at two or more different temperatures should permit the evaluation of A and E_a in the Arrhenius relationship.

$$k = A.\exp[-E_a/RT]$$

Where, k = the rate constant; A = the frequency factor.

E_a being a direct measure of reactivity in the sense that it measures the magnitude of the activation energy barrier that must be surmounted for hydration to proceed. Regourd et al [7] have applied this approach to blended cements with some degree of success, although it should be noted that the validity of applying such assumptions to heterogeneous reactions in highly viscous media should only be considered with caution. The method however may be promising as a means of determining pozzolanic (or slag) activity.

Most of the reported studies of hydration that employed conduction calorimetry have been concerned with detailed investigations of Portland cement hydration alone or in the presence of reaction modifiers such as sulphates [4,6]. Some recent studies have been conducted on blended cements mostly those containing fly-ash [9,10] or granulated blastfurnace slags [7,11,12,13]. Roper, Kam and Auld [14] have used conduction calorimetry to study the early heat of reaction of slag / $Ca(OH)_2$ and slag / portland cement mixes. Other authors have reported the use of calorimetry in examinations of the hydration reactions

of cements containing silica fume [15,16,17].

3. Methods of Measurement.

The standard methods [8] used to measure heat of hydration employ Hess' law of heat summation and measure the difference between the heat of solution of anhydrous cement and cement hydrated for seven and twenty-eight days. The method gives integrated heats of hydration for periods over three days but gives no information on the progress of early reactions. However this is not the most serious limitation with regard to its use. When applied to blended cements the method has an inherent source of error because not all of the supplementary cement is soluble in the acidic medium used. This is particularly serious in that the products of hydration may be soluble and hence a systematic under-estimation of the heat of reaction is inevitable. It is probably true to generalize that this method is not applicable to the determination of heats of hydration of cements containing fly-ash, blastfurnace or non-ferrous slags or silica fume, each of which contain substantial proportions of components that are not soluble in acid but are soluble and reactive in alkaline media.

Because most cements, including those containing supplementary cementing materials, produce most of their heat of hydration during the first three days of reaction a continuous record of the process can be useful for the reasons discussed in previous paragraphs. In the field, cement hydration occurs in circumstances that are rarely either isothermal or adiabatic. Thus it is open to choice as to which state is selected for research purposes. Adiabatic measurements are of limited value because uncertainties as to the effects of temperature on the nature and relative proportions of the products of hydration render the data difficult to interpret.

Conduction calorimetry is performed under near-isothermal conditions, the temperature of the reacting materials never rising more than 0.5 to 1.0 ^{o}C above the surroundings. The first conduction calorimeter was made by Tian [18] and a similar device was used by Carlson in 1933 [19] to investigate cement hydration. Stein [20] developed and used a conduction calorimeter to examine the effects of organic additives on cement hydration and to examine the retardation of C_3A hydration by gypsum. Other instruments have recently been developed and have been applied by various workers to problems related to cement hydration [21,22,23,24,25].

The simplest and one of the most widely used conduction calorimeters was developed at the British, Cement and Concrete Association Laboratories and was originally described by

Forrester in 1970 [5]. A subsequent description of its application to studies of the effects of sulphate on the hydration of cement was presented by Smith and Matthews [6]. Recently its use has become more frequent and it has been employed extensively by Pratt and co-workers for studies of cement chemistry [9,17]. It is frequently called the Wexham Instruments calorimeter.

An early version of the Wexham Instruments calorimeter is shown diagrammatically in Figure 3 (reproduced from [5]). Later versions have been subject to some modification but the basic principles of operation of the instrument remain the same. Major modifications and simplification of construction have been made by researchers at Ontario Hydro [26]. The following description of the principles of the calorimeter are taken from Forrester's original publication, supplemented with comments and observations drawn from the report of Smith and Matthews and the experience of the present author.

The hydrating cement is placed in a polyethylene bag in an aluminum can containing oil and a calibration heater. The can rests upon six modified Hatfield-Turner conduction discs that in turn rest upon an aluminum heat sink. The whole cell system is surrounded by foam insulation, contained in an acrylic cylinder and operates immersed in a constant temperature water bath. Because the heat of reaction is conducted away continuously the calorimeter effectively operates isothermally. The following paragraphs serve to outline the principles of the operation of this calorimeter and indeed apply to most other forms of conduction calorimetric measuring devices.

Consider the calorimeter to be at constant temperature with the inner temperature T_i equal to the sink temperature T_o. Consider the development of a small quantity of heat dW over a short time interval dt in the calorimeter cell. The result is that the temperature of the inner container is raised by an amount T, such that:

$$T = T_i - T_o.$$

If the heat capacity of the inner can and its contents is u, then internal heating will absorb energy at the rate:

$$u.\ dT/dt$$

Heat in excess of this will be conducted through the heat sink at a rate proportional to T, thus:

$$\text{rate of heat loss} = pT$$

The heat balance for the system then can be written:

$$dW/dt = pT + u.dT/dt \quad \text{---------- [1]}$$

The conduction discs produce an EMF that is proportional to the temperature difference T, such that:

$$E = gT$$

Thus:

$$dE/dt = g.dT/dt \quad \text{---------- [2]}$$

and $dW/dt = p/g.E + u/g.dE/dt$

or $dW/dt = K_1.E + K_2.dE/dt \quad \text{------- [2]}$

where K_1 and K_2 are constants.

Measurement of E and dE/dt at different values of t, together with determination of the calorimeter constants by calibration, allow for a plot to be made of rate of heat evolution versus time throughout the entire hydration sequence. Integration of these data provides a measure of the heat of reaction (hydration) over any cumulative period.

Calibration of the system is performed electrically when heat evolution from the cement has reduced to a small and steady rate. A small amount of stable electrical power is supplied to the calibration heater and the heat generated causes the conduction discs to respond as shown in Figure 4.

Because the calibration is performed in the presence of the reacting materials without disturbing the cell it can be assumed that there is no difference in thermal "mass" between the materials during hydration and at the time of calibration. thus if the rate of producing heat during calibration is known (ie if the heater Wattage is known) K(1) and K(2) can be determined from

measurements of the slope and maximum height of the calibration curve.

The entire procedure of measuring the rate time curves for both experimental and calibration steps and the integration of the output data can be automated by a simple microprocessor link using a personal computer or other suitable device. The output from the cell is in the form of a DC signal in the range 0-100mV that can readily be supplied to a measuring device such as a digital voltmeter (DVM) from which a digital signal can be withdrawn as required though a suitable interface.

Figure 5. shows a schematic representation of the components required to operate a simple conduction calorimeter under microprocessor control with automatic collection and processing of the output data.

A system of this type, using a CBM PET computer is in operation at the Ontario Hydro laboratories in Toronto where four calorimeter cells are operated consecutively for the determination of heat of hydration on a routine basis [26].

REFERENCES.

1. Collings, R.K. and Wang, S.S.B.; Private communication of data from CANMET report in preparation.

2. Skalny, J. and Brophy, J.E.; "Hydration of Portland and Blended Cements". Preprint prepared for Int, Conf. on Slag and Blended Cements, 18-19 Feb. 1982, Birmingham, Alabama.

3. Skalny, J., Jawed, I. and Taylor, H.F.W.; World Cement Technology, Sept. 1978, 183-195.

4. Lerch, W.; Proc. ASTM, 46, 1252-1292, (1946)

5. Forrester, J.A.; Cement Technology, 1 (3), 95, (1970)

6. Smith, M.A. and Matthews, J.D.; Cement and Concrete Research, 4, 45-55, (1974).

7. Regourd, M., et al; "Characterization and thermal activation of slag cements". Proc. 7th. Int. Congr., Chemistry of Cements, Paris 1980, Paper III-105.

8. ASTM C186-68. (Note: For a discussion of heats of hydration and their determination see Lea F.M. "The Chemistry of Cement and Concrete", pp 290-297, 3rd edn. Chem. Pub. Co. 1971)

9. Halse, Y. and Pratt, P.L.; "The Development of Microstructure During the Hydration of Cement Blends I. OPC with 30% of Drax P.F.A."; Paper presented at 1st Int. Conf. "Flyash, Silica Fume, Slag and Other Mineral By-products".

10. Costa, U. and Massazza, F.; "Some Properties of Pozzolanic Cements Containing Fly Ashes". Paper in "Fly ash, Silica fume, Slag and other mineral byproducts in concrete - Vol I.", ACI special publication SP-79, pp 235-254, 1983.

11. Daimon, M.; "Mechanism and Kinetics of Slag Cement Hydration". Proc. 7th. Int. Congr., Chemistry of Cements, Paris 1980, Paper III-2/1.

12. Kondo, R., et al ; J.Am.Ceram.Soc., 59, 848-851,(1980).

13. Regourd, M.; "Structure and Behavior of Slag Portland Cement Hydrates". Proc. 7th. Int. Congr., Chemistry of Cements, Paris 1980, Paper III-2/10.

14. Roper, H., Kam, F., Auld, G.J.; "Characterization of a copper slag used in mine fill operations". Paper in "Fly ash, Silica fume, Slag and other mineral byproducts in concrete - Vol II.", ACI special publication SP-79, pp 1092-1109, 1983.

15. Lessard, S., Aitcin, P.C. and Regourd, M.; "Development of Low Heat of Hydration Blended Cement". Paper in "Fly ash, Silica fume, Slag and other mineral byproducts in concrete - Vol II.", ACI special publication SP-79, pp 747-763, 1983.

16. Meland, I. "Influence of Condensed Silica Fume and Fly Ash on the Heat Evolution in Cement Pastes". Paper in "Fly ash, Silica fume, Slag and other mineral byproducts in concrete - Vol II.", ACI special publication SP-79, pp 665-676, 1983.

17. Goult, D.J. and Pratt, P.L.; "The Development of Microstructure During the Hydration of Cement Blends II. Low Alkali Sulphate-resistant Cement with Silica Fume."; Paper presented at 1st Int. Conf. "Flyash, Silica Fume, Slag and Other Mineral By-products".

18. Tian, A.; Bull. Soc. Chim. Fr. 33,(4), 427-429, (1923).

19. Carlson, R.W.; Proc.ASTM. 34, Pt.2, 322-328, (1934).

20. Stein, H.N.; J. Appl. Chem. 11,(12), 474-492, (1961).

21. Antoniou, A.A. and Litvan, G.G.; Rev. Sci. Instruments, 38, (11), 1641-1644,(1967).

22. Monfore, G.I. and Ost, B.; J. PCA Res.& Dev. May, 1966, pp

13-20.

23. Kantro, D.L.; ASTM Jnl. of Testing and Evaluation,3,(4), 312-321, (1975).

24. Adams, L.D.; Cement and Concrete Research, 6, 293-308, (1976).

25. Wu, X., Roy, D.M. and Langton, C.A.; Cement and Concrete Research, 13, 277-286, (1983).

26. Hooton, D. ; Private Communication.

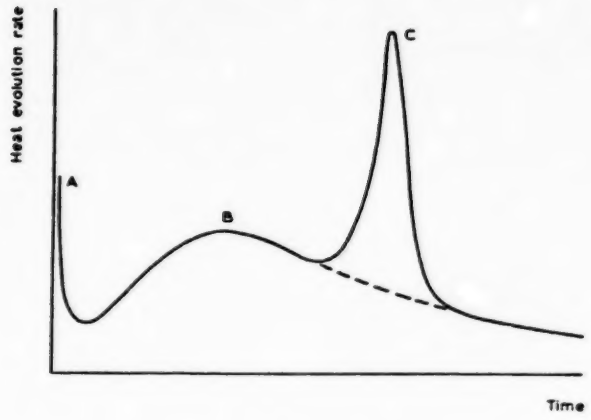


Figure 1. Schematic form of heat evolution curve for Portland cement. (From reference [5]).

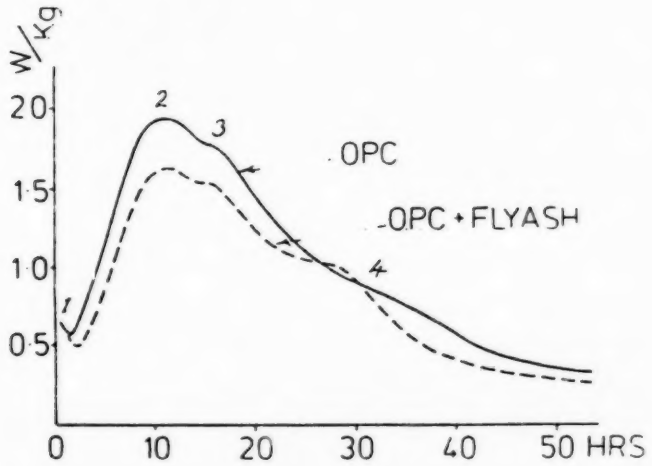


Figure 2. Effect of fly-ash on the heat evolution from Portland cement. (From reference [9]).

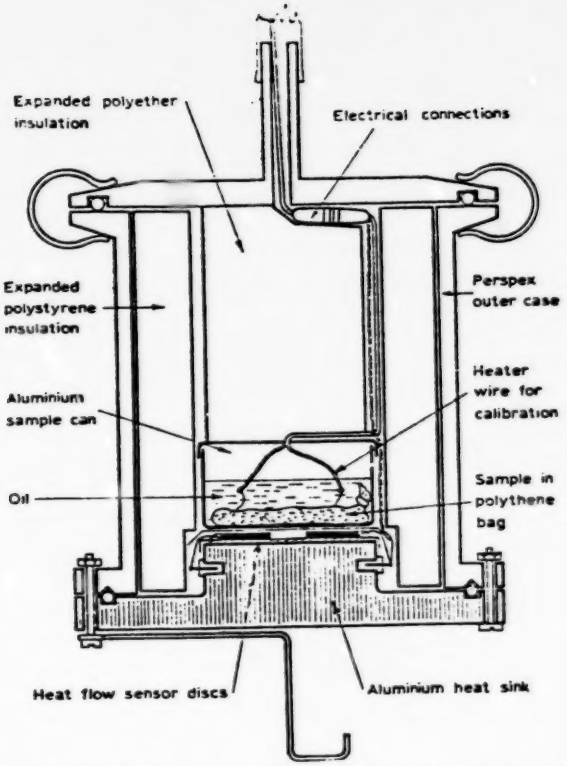


Figure 3. Schematic representation of an early version of the Wexham Instruments Calorimeter. (From reference [5]).

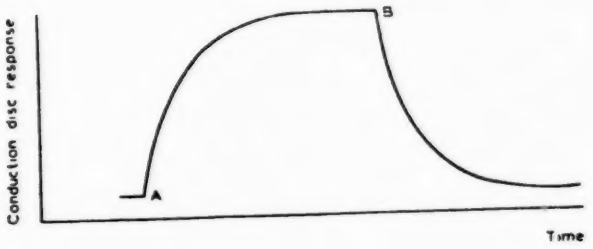
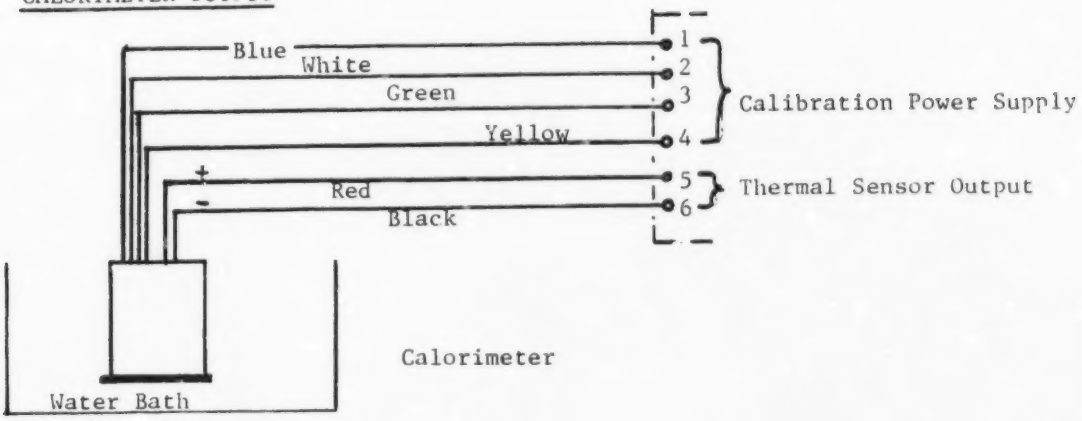
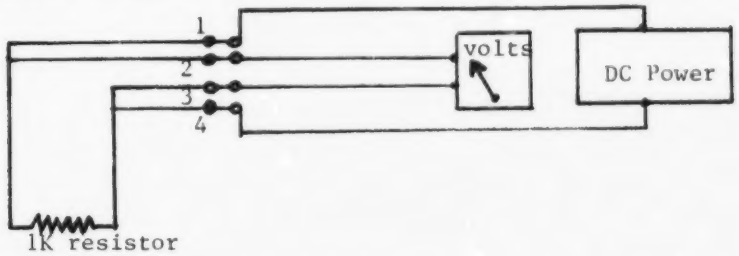


Figure 4. Typical form of calibration curve from the Wexham Instruments Calorimeter. (From reference [9]).

CALORIMETER OUTPUT



CALIBRATION POWER SUPPLY



THERMAL SENSOR OUTPUT AND MEASURING DEVICES

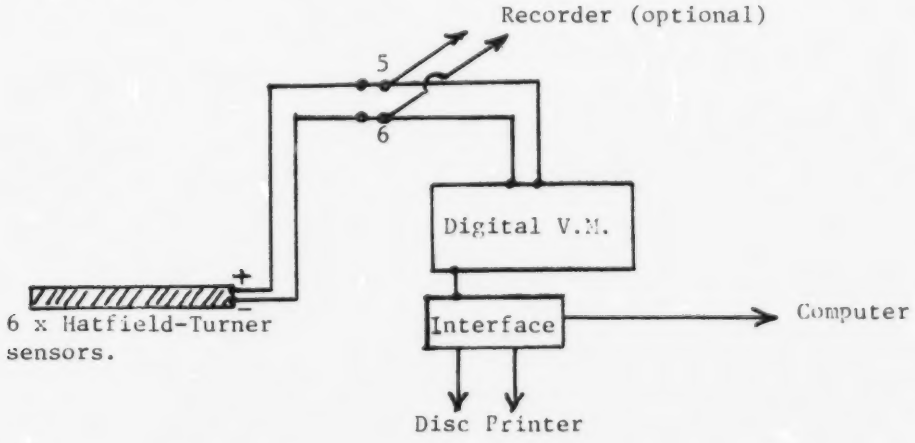


Figure 5. Schematic wiring diagram for connection of a Wexham Instruments Conduction Calorimeter to calibration and measuring devices.